

REMARKS

This is in response to the Office Action dated November 2, 2007. In view of the foregoing amendments and following representations, reconsideration is respectfully requested.

Initially, Applicants note that a new oath is enclosed, curing the defect kindly pointed out by the Examiner in the last Office Action.

Upon entry of this amendment, claims 1, 3-5, and 7-8 are pending in the application. Claims 1, 4, 5, 7, and 8 have been amended. Claims 2 and 6 have been cancelled. ***No new matter has been added.*** Support for this amendment may be found on pages 1, 7-8, and 10-11 of the written disclosure and Figures 1 and 2.

Applicants note that a number of editorial amendments have been made to the specification and abstract for grammatical and general readability purposes. Due to the number of changes made, a substitute specification and abstract are submitted herewith. No new matter has been added. Also enclosed is a marked-up copy of the original specification and abstract showing the changes incorporated into the substitute specification and abstract.

Claim Rejections under 35 U.S.C. §102

On pages 2-3 of the Office Action, original claims 1-8 were rejected under 35 U.S.C. § 102(b) as being anticipated by U.S. Patent 4,032,618 to Matthews. Applicants respectfully traverse this rejection on the following basis.

For at least these reasons, it is submitted that the present invention, as embodied by the current claims, is patentably distinguishable over the Matthews reference.

Matthews discloses a purification system comprising a heat exchanger (32) and a water scrubber (18). The heat exchanger (32) and water scrubber (18) of Matthews, however, do not correspond to the cooling tower and cleaning tower of the claimed invention, which are coupled such that make-up water used in the cleaning tower can be delivered to the cooling tower, enabling ammonia absorption in both towers.

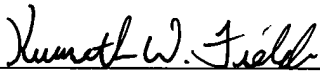
Further, the purification method disclosed by Matthews, like the conventional methods discussed in the disclosure (see p. 1-5) of the present application, employs a sulfided catalyst to

remove ammonia (Matthews, Col. 3, lines 24-50). As noted in the disclosure, chemicals tend to be expensive, difficult to manipulate, and may emit polluting by-products. The present invention, however, utilizes water ("make-up water") to absorb and remove ammonia; i.e. "water-washing." To this end, make-up water is charged into an ammonia-rich gas in *both* a cooling step (occurring in a cooling tower) and a cleaning step (occurring in a cleaning tower). Matthews fails to teach or suggest introducing make-up water as an absorbent in a cleaning step and sending a portion thereof to an upstream cooling step. What is more, Matthews does not contemplate reducing the concentration of ammonia to 10 ppm or less by controlling the amount of make-up water introduced in the cleaning step. The subject matter of claims 1 and 5 is therefore novel in view of Matthews. Also, claims 3-4 and 7-8 are allowable at least by virtue of their dependency on claims 1 or 5.

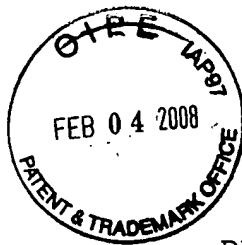
In view of the above, reconsideration and allowance of this application are now believed to be in order, and such actions are hereby solicited. In the event that the Examiner has any comments or suggestions of a nature necessary to place this case in condition for allowance, then the Examiner is encouraged to contact the Applicant's undersigned attorney by telephone to promptly resolve any remaining matters.

Respectfully submitted,

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DESCRIPTION

WET GAS PURIFICATION METHOD AND SYSTEM

5 | BACKGROUND OF THE INVENTION~~Technical Field~~

The present invention relates to a wet gas purification method for removing ammonia from a gas. More particularly, the present invention relates to a wet gas purification method and a wet gas purification system suitable for removing
10 ammonia from a gas such as a coal or heavy oil gasification gas.

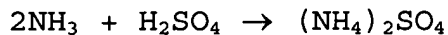
| ~~Related Art~~

Conventionally, in a wet purification system for a coal
15 or heavy oil gasification gas, sulfuric acid is added upstream of an ~~H₂S~~ a hydrogen sulfide (H₂S) absorption tower as a pH adjuster. This allows for the removal of ~~NH₃~~ ammonia (NH₃), which is a source of fuel NO_x in gas turbines, during the water-washing step for removing impurities in the gas.

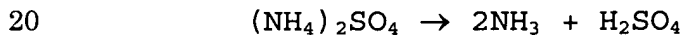
20 Specifically, if a gas containing ammonia is burned in a gas turbine without being purified, the gas becomes a NO_x source, so that it is necessary to recover as much ammonia as possible. To absorb the ammonia, a method for decreasing the

pH of an absorbent in a water-washing tower is carried out, by which most of the ammonia can be removed. As a pH adjuster, sulfuric acid is preferably used in adjusting alkali of ammonia. The pH of the water-washing tower can be reduced by
5 the addition of the sulfuric acid.

The ammonia removed in the above-described water-washing step is taken out by an ammonia stripper. Since sulfuric acid is added to the absorbent, ammonium sulfate exists in the discharged solution from the ammonia stripper. The ammonia is
10 recovered as aqueous ammonium sulfate.



To expel ammonia components from the aqueous ammonium sulfate and to recover ammonia as aqueous ammonia by a stripping method, caustic soda (NaOH) is added before the
15 stripping. Usually, the caustic soda is charged into a neutralization tank provided upstream of the stripper and is mixed. Then, the mixed liquid is sent to the stripper. The addition of NaOH yields sulfuric acid and ammonia again as described in the following formula. Then ammonia is recovered.



On the other hand, in the above-described conventional system, one of major reasons for adding sulfuric acid is to facilitate the operation control of the system. That is to

say, if the pH value of the liquid is decreased by sulfuric acid, ammonia can be recovered and removed. There is no need for monitoring and controlling the amount of ammonia at the following step of the water-washing step, and the control of pH suffices for operation. Because of such ease of operation, a method in which sulfuric acid is added has been used.

Also, by decreasing the pH value, hydrogen sulfide is not removed in the water-washing step, but passes through easily. A higher pH value presents a disadvantage of dissolution of hydrogen sulfide in the liquid, ~~so that making~~ the treatment of effluents ~~is complicated. Therefore,~~ ~~in~~Specifically, the conventional ~~step,~~ practice involves changing the pH value between the separation/removal step of ammonia and the removal step of hydrogen sulfide ~~are separated~~ by ~~changing the pH value so that in the ammonia separation~~ step, hydrogen sulfide does not dissolve in the liquid, and is not removed from the gas.

~~However, in such a~~ Moreover, the conventional ~~step, a~~ ~~step for adding~~ practice requires the addition of sulfuric acid and caustic soda, which are costly ~~is needed, so that the~~ operation cost ~~increases due to the addition of these~~ chemicals. ~~Specifically, in order~~ For example, to treat 1000 ppm of ammonia existing in the gas, 1/2 mole of sulfuric acid

is needed for every 1 mole of ammonia, which increases the chemical cost. Also, in order to treat the nitrogen components in the effluent from a water-washing tower, which contains absorbed ammonia, at least 2 moles of caustic soda (NaOH) are required per 1 mole of sulfuric acid. Further, an amount of caustic soda equivalent to the amount of ammonia is needed. Therefore, the chemical expense is great. Thus, while the ammonia can be recovered, the after-treatment steps are complicated and increase in number.

Further, since the recovered aqueous ammonia accounts for about 20 percent by weight, there is no other choice but to treat it as waste, which poses a problem of treatment cost.

SUMMARY OF THE INVENTION~~Disclosure of the Invention~~

In view of the above problems, the inventors carried out studies to develop a method for purifying an ammonia-containing gas in which chemicals such as sulfuric acid and caustic soda, which have been regarded as necessary, are not used at all, by which the running cost involved in operation is reduced, emissions are restrained effectively, the manipulation step and system are simple and the operation is easy, and the reliability is high thereby significantly reducing operation cost and effectively restraining emissions.

Furthermore, the steps and system are simple, operation is easy, and reliability is high.

As a result, the inventors arrived at the present invention through their discovery that the above problems can be solved by continuously measuring the concentration of ammonia in the gas after the washing step, and controlling the charging makeup water in the washing step, rather than adding ~~in place of the conventional addition of sulfuric acid so that~~ to reduce the ammonia concentration is to 10 ppm or lower.

Specifically, the present invention provides a wet gas purification method for removing ammonia in the gas comprising: a water-washing step for absorbing ammonia in the gas into absorbent to remove the ammonia; and an ammonia treating step for stripping the ammonia from the absorbent to be discharged after the water-washing step to separate an off-gas containing ammonia from effluents, wherein, makeup water is charged continuously or intermittently in the water-washing step so that the concentration of the ammonia is 10 ppm or lower after the water-washing step. The washing step may comprise a cooling step and a cleaning step. That is to say, the partial pressure of NH_3 can be decreased by decreasing the concentration of ammonia in aqueous solution, rather than by actively controlling the pH value, to keep the NH_3 absorbing

performance.

In the present invention, it is preferable that the method further comprises a step for burning the off-gas. By this off-gas burning step, hydrogen sulfide dissolved in the water-washing step can also be decomposed simultaneously with the decomposition of ammonia.

Further, in the present invention, it is preferable that effluents in the ammonia treating step be circulated charged to the washing step as makeup water.

In the present invention, even if hydrogen sulfide is dissolved in the absorbent, it can be separated to be removed from the liquid by a stripper, so that there is no need for treating hydrogen sulfide in the liquid. The off-gas containing ammonia and hydrogen sulfide can be treated by being burned in the combustion furnace at a following step. It is efficient for the total system to burn the off-gas using a regenerative combustion furnace or a direct burning combustion furnace for burning the off-gas coming out of a hydrogen sulfide absorbing step. According to the present invention, charging only makeup water can make ammonia stripping easy. Further, the discharged substance can be easily used for combustion treatment.

According to the present invention, since only makeup

water is charged, and neither sulfuric acid nor caustic soda is used, the cost required for operation can be reduced significantly, and also the manipulation step can be made simple and easy.

5 Since the makeup water is added, ammonia can exist in the form of ammonium carbonate $(\text{NH}_4)_2\text{CO}_3$ by the action of existing carbon dioxide. When the accumulated $(\text{NH}_4)_2\text{CO}_3$ is heated and the temperature rises, the $(\text{NH}_4)_2\text{CO}_3$ can release carbon dioxide to yield ammonia again. By stripping ammonia
10 NH_3 and carbon dioxide (CO_2) without using NaOH in this manner, the cost required for operation can be reduced. Also, by burning H_2S and NH_3 in the effluent stripping gas, the cost for treating aqueous ammonia can be eliminated.

 The present invention is explained in detail below with
15 reference to an embodiment. The scope of the present invention is not limited by this embodiment.

BRIEF DESCRIPTION OF THE DRAWINGS~~Brief Description of the~~
Drawings

20 FIG. 1 is a schematic view showing the outline of a system suitable for a wet gas purification method in accordance with the present invention;

 FIG. 2 is a schematic view showing a configuration of a

purification system used in Example 1; and

FIG. 3 is a graph in which the concentration of ammonia in a gas discharged from the outlet of a cleaning tower is plotted against the amount of makeup water.

5 In the above figures, reference numeral 1 denotes a gas cooling tower, 2 denotes a gas cleaning tower, 3 denotes a flash drum, 4 denotes an ammonia stripper, 5 denotes an off-gas fired furnace, and 7 denotes a circulating pump.

10 DETAILED DESCRIPTION OF THE INVENTION~~Best Mode for Carrying~~
out the Invention

A specific embodiment of a wet gas purification method in accordance with the present invention will now be described with reference to the attached drawings.

15 FIG. 1 is a schematic view showing one example of a system suitable for a wet gas purification method in accordance with the present invention. In the system of the embodiment, a water-washing step may comprise a cooling step and a cleaning step. The cooling step may be performed by a
20 gas cooling tower 1, and the cleaning step may be performed by a gas cleaning tower 2. Makeup water for absorbing ammonia components in a gas is continuously or intermittently charged into the gas cleaning tower 2. By these two water-washing

towers, ammonia in the gas can be absorbed in an absorbent, and thereby removed. The amount of the makeup water to be charged is controlled so that the concentration of ammonia in the gas is 10 ppm or lower after the water-washing step. The
5 gas discharged from the gas cleaning tower 2 is sent to a hydrogen sulfide absorption tower.

In the washing step of the embodiment, ammonia in the gas is removed by adding makeup water without adding sulfuric acid for adjusting the pH value. The washing step (carried in
10 the water-washing tower) consists of two steps, which use two towers: gas cooling tower 1 and the gas cleaning tower 2. The makeup water charged into the gas cleaning tower 2 can be circulated by a pump 7 and acts as the absorbent for absorbing ammonia. Some of The towers are coupled such that a part of
15 the absorbent is sent into the gas cooling tower 1 provided upstream of the gas flow direction, and is circulated by a pump 7 direction. A pump 7 circulates absorbent in the gas
cooling tower 1 as well.

Conventionally, in the gas cooling tower 1, a step of
20 adding sulfuric acid has been carried out. In the embodiment, makeup water is introduced into the gas cleaning tower 2 in place of sulfuric acid. Thereby, the concentration of ammonia in the absorbent in the whole of the washing step is decreased,

and ammonia is removed. Specifically, when the concentration of ammonia in the absorbent becomes high, the absorbent tends to release ammonia due to partial pressure. Thus, it becomes difficult to remove ammonia using the absorbent in view of
5 reaction equilibrium. Therefore, supplying makeup water continuously or intermittently can keep absorbent in a state of being able to absorb and remove ammonia.

Supplying makeup water in such a way allows the ammonia to react with carbon dioxide in the gas to dissolve in the
10 absorbent as ammonium carbonate. Ammonia is more easily stripped in this state, since the pH value of the absorbent is high compared with when sulfuric acid is also present. Thus, ammonia and carbon dioxide can be taken out of the absorbent by raising the temperature of an ammonia stripper provided
15 downstream of the water-washing towers without requiring the addition of caustic soda.

In the system the absorbent may be water (H_2O). The circulation of the absorbent in the water-washing towers by the operation of the system results in the increased
20 concentration of ammonia in the absorbent. As described above, in the embodiment, a gas cooling tower 1 and gas cleaning tower 2 can be provided. By these two-towers, the concentration of ammonia can be made low at the outlet of the

gas cooling tower 1. Thus, water containing less dissolved components can always be circulated in the gas cleaning tower 2, so that ammonia can be absorbed to be removed effectively.

However, the washing step need not necessarily be
 5 provided with two towers as in the embodiment. A water-washing tower consisting of one-tower can also be used. Inside of the one tower can be divided into two, and gas cooling and gas cleaning can be performed in the one tower. In the tower, liquids at the upper part and lower part which
 10 can be divided by a tray etc. are circulated separately.

~~Charging makeup water is carried out so that the~~ The
 concentration of ammonia in the charged yielded gas is successively monitored, and an amount of makeup water best suitable for the amount of ammonia each time can be charged. The monitoring of the amount of ammonia can be performed, for example, by measuring the concentration thereof in the yielded gas just before the gas cooling tower 1.
 15

~~The monitoring of the amount of ammonia can be performed, for example, by measuring the concentration thereof in the yielded gas just before the gas cooling tower 1.~~
 20

On the other hand, ammonia in the a gas, which is charged ~~into, for example,~~ into a gas turbine must be reduced as far much as possible because the ammonia is responsible for

fuel NOx generation. ~~For example, when the concentration of ammonia is reduced to 10 ppm or lower,~~ In such case, the amount of charged makeup water is should be controlled to- achieve the concentration reduce the concentration of ammonia
5 to 10 ppm or lower. Therefore, it is usually preferable that the operation be performed by monitoring the concentration of ammonia in the gas near the outlet of the gas cleaning tower 2 at the later stage of water-washing step and by checking that the concentration of ammonia has a value not higher than a
10 fixed value.

~~For the absorbent~~ Absorbent is discharged from the water-washing step, some of ~~the absorbent~~ which is usually drawn from the absorbent circulating in the gas cooling tower
1 ~~is usually~~ and sent to the ammonia stripper 4 via a flash
15 drum 3. In the stripper 4, ammonia is stripped from the ~~absorbent in which ammonia has been absorbed.~~ Then, the absorbent is divided into an off-gas containing ammonia and the remaining washing liquid. The ammonia stripper 4 is usually operated at about 80°C at the upper stage and at about
20 130°C at the lower stage.

Also, in this stripper 4, hydrogen sulfide components contained in the absorbent are also removed, and are contained in the off-gas together with ammonia. Therefore, the liquid

after stripping does not contain hydrogen sulfide. Such an off-gas containing ammonia and a minute amount of hydrogen sulfide is sent into an off-gas fired furnace 5, whereby the ammonia and hydrogen sulfide are simultaneously burnt.

5 According to the above-described embodiment, the amount of effluent is increased by the charge of makeup water. Therefore, it is preferable that the effluent in the ammonia treating step be used by circulation as the makeup water charged in the washing step.

10 A system in which the water coming out of the stripper 4 is used again as makeup water is advantageous because the amount of water treated finally as effluent does not increase as in the conventional example. Also, the system is preferable in terms of the ease with which makeup water can be
15 secured. Since the water discharged from the stripper 4 usually has a temperature increased to 100°C or higher, the water may be supplied into the gas cleaning tower 2 as makeup water after being cooled.

 The gas to be purified in the present invention may be
20 any gas containing ammonia. Specifically, for example, the gas includes, but is not limited to, coal gasification gas containing much ammonia and hydrogen sulfide.

 The gas purification method in accordance with the

present invention can suitably used as a wet purification method for coal gasification gas at the preceding step of a hydrogen sulfide removing step as part of a system in which coal is gasified and used as power generation fuel. By the use of the above-described purification method in accordance with the present invention, purification can be performed very efficiently in the system for treating ammonia-containing gas.

According to the treating method in accordance with the present invention, since neither sulfuric acid nor caustic soda is used, the cost required for operation can be reduced significantly. Also, since ammonia is accumulated as $(\text{NH}_4)_2\text{CO}_3$, NH_3 and CO_2 are stripped by increasing the temperature without the use of NaOH , by which the cost required for operation can be reduced.

On the other hand, HCN components, which are other harmful components contained in the gas, cannot be absorbed and removed unless the absorbent has a high pH value. HCN components are scarcely removed by an absorbent having a pH value of about 5 to 6. In the conventional method in which sulfuric acid is added, the pH value of absorbent decreases (to about pH 5 to 6). By contrast, in the present invention, the pH value of absorbent in the water-washing towers increases (to about pH 6 to 9). Therefore, according to the

purification method in accordance with the present invention, the HCN removing performance is improved by the increase in pH value of absorbent to about 6 to 9.

Also, according to the present invention, causes of
5 material corrosion can be reduced by the increase in pH value of absorbent in the water-washing towers and the decrease in concentration of chlorine in the absorbent due to the addition of makeup water.

The experimental results showing the advantageous
10 effects of the present invention will now be explained in detail as an example. However, the present invention is not limited by the example.

Example 1

FIG. 2 shows the outline of a system in example 1.

15 Two towers are provided: the gas cooling tower 1 is provided upstream of the flow of gas, and the gas cleaning tower 2 is provided downstream of the flow of gas. From the inlet of the gas cooling tower 1, a yielded gas having an ammonia concentration (y_0) of 1200 ppm was introduced at a gas
20 flow rate of 3500 m³N/h under a pressure of 0.9 MPa.

The amount (x kg/h) of makeup water charged into a circulation line of the gas cleaning tower 2 was changed continuously in the range of 40 to 350 kg/h.

When the temperatures of both of the gas cooling tower 1 and the gas cleaning tower 2 were set at 40°C, as shown in FIG. 3, the ammonia concentration (y2) measured at the outlet of the gas cleaning tower 2 decreased as the amount of makeup water increased. The amount of makeup water in this example indicates the amount in a preliminary plant. From the results, it was found out that if the amount of makeup water charged in the washing step is increased the concentration of ammonia in the yielded gas can be decreased very effectively.

The above is a description of the embodiment and example of the present invention. The embodiment and example are provided to aid in understanding the present invention, and do not limit the scope of the present invention.

ABSTRACT

~~—The present invention provides a wet gas purification method in which ammonia in the gas is removed, and a system for carrying out said method, characterized in that the method includes a washing step in which ammonia in the gas is absorbed in an absorbent for removal; and an ammonia treating step in which ammonia is stripped from the discharged absorbent at a following stage of the washing step, wherein the absorbent is divided into an off gas containing ammonia and effluent. In the washing step makeup water is charged continuously or intermittently so that the concentration of ammonia in the gas having passed through the washing step is 10 ppm or lower. According to the present invention, a wet gas purification method can be performed in which the running costs involved in operation is reduced, the manipulation step and system are simple, operation is easy, and the reliability is high.~~

A wet gas purification method is provided for removing ammonia from a heavy oil gasification gas, such as coal. The method principally involves a washing step during which absorbent is charged into the gas to absorb ammonia and an ammonia treating

step wherein absorbent discharged from the washing step is
separated into an effluent and an off-gas containing ammonia.
The amount of absorbent charged during the washing step is
controlled such that the ammonia concentration of gas exiting
5 the washing step is 10ppm or less.

FIG. 1

1: ~~YIELDED GAS~~

2: ~~TO H₂S ABSORPTION TOWER~~

3: ~~MAKEUP WATER~~

5 4: ~~COMBUSTION IMPROVER~~

5: ~~EXHAUST GAS TREATMENT EQUIPMENT~~

6: ~~COMBUSTION AIR~~

FIG. 2

10 ~~TO H₂S ABSORPTION TOWER~~

~~MAKEUP WATER~~

~~EFFLUENT TREATMENT EQUIPMENT~~

FIG. 3

15 ~~NH₃ CONCENTRATION AT OUTLET OF CLEANING TOWER (y ppm)~~

~~MAKEUP WATER (x kg/h)~~